

**Process for the transesterification of fat and/or oil
by means of alcoholysis**

5 This invention relates to a process for obtaining fatty acid esters from triacyl-
glycerides by means of alcoholysis. In particular, the invention relates to a process
for the transesterification of fat and/or oil by alcoholysis wherein, in order to
accelerate the process, in the initial stage at least one alkanol fatty acid ester is
10 added in a quantity such that the reaction mixture produced thereby consists of
one phase.

Transesterification reactions are known per se. They are a commercially important
class of industrial organic reactions. In a transesterification reaction, an ester is
15 converted into a different ester by exchange of the acid groups or by exchange of
the alcoholic groups. If the transesterification is carried out by exchange of the
alcoholic groups, it is termed alcoholysis (also alkanolysis). In alcoholysis, the
alcohol or the alkanol is added in excess in order to obtain a high yield of the
desired ester. Recently the production of alkyl esters, in particular of methyl
20 esters, from vegetable oils (for example, rapeseed oil, soybean oil) has become
extremely topical in connection with the production of diesel fuel from renewable
raw materials.

Transesterification is an equilibrium reaction which is usually initiated simply by
25 mixing the reactants. The reaction proceeds so slowly, however, that a catalyst is
usually necessary in order for the reaction to be carried out commercially. Strong
acids or strong bases generally serve as catalysts.

Fats and oils consist mainly of glycerides (mono-, di- and triglycerides). In the
30 transesterification of such fats and oils, low-molecular monohydric alcohols can be
substituted for the glycerol component. Here, the method of Bradshaw (described
in US Patents 2,271,619 and 2,360,844) is frequently employed in practice. The
reaction is carried out in an open vessel, which can consist of ordinary carbon steel.
The fat or oil must be dry (moisture-free), clean and above all neutral, i.e. the
35 content of free fatty acids must be negligibly low (acid value not higher than 1.5).
In general, the monohydric alcohol is added in large excess to the reaction mixture
in order to increase the yield and the reaction rate (the equivalent ratio is often
greater than 1:6).

In a paper by Wright et al. (H.J. Wright, J.B Segur, H.V. Clark, S.K. Coburn, E.E. Langdon and R.N. DuPuis, Oil & Soap, **21** [1944] 145-148), the precise conditions for the alcoholysis of fats with methanol and ethanol were investigated in detail. The authors also describe experiments with alcoholysis using other monohydric alcohols. It is explained that the above-mentioned alcoholysis catalysed by alkali is completely successful only if the fat is virtually free of free fatty acids and the reaction mixture is free of water. If one of these conditions is not met, saponification takes place; this results in a loss of alkalinity and in the formation of a gel structure, which prevents or retards the separation and precipitation of the glycerol.

The transesterification of the triacylglycerides by means of alcoholysis is characterised in that the reaction between alkanol and triacylglycerides requires an induction stage, during which there is only a low reaction rate, because the alkanol reaction component is not soluble in the oil. This situation is very troublesome especially during the production of methyl esters, because methanol is only slightly soluble in the oils and fats which are to be transesterified. However, methanol is readily soluble in the methyl esters of the fatty acids. Owing to the low concentration of methanol in the oil, the transesterification reaction only proceeds slowly. The reaction mixture has to be mixed vigorously until ultimately the ester content has increased to such an extent that the reaction mixture consists of one phase and the reaction rate suddenly rises considerably.

In practice, alkali metals or alcoholates of the alkali metals are used as catalysts. The alkaline catalysts dissolve in the reaction mixture, i.e. the reaction is catalysed homogeneously. During the reaction, the alkali metals and their alcoholates are converted to soaps, which dissolve particularly in the glycerol formed and increase the cost of its further processing in order to obtain pure glycerol. However, the methyl ester also retains small quantities of alkali, which may not be completely without problems where methyl esters are used as diesel fuel. Because of this, heterogeneously catalysed processes have also been proposed recently; for example, using a metal salt of a strongly basic amino acid as a solid catalyst which is insoluble in the reaction mixture (Patent Application DE 199 50 593 A1). Furthermore, a catalyst based on titanium oxides has been developed, the disadvantage of which is that the reaction temperatures are in the region of 240°C.

Proceeding from this prior art, the object of the invention is to eliminate or to shorten this induction stage while maintaining moderate reaction temperatures and thereby to render the process more effective.

This object is achieved by a process for the transesterification of fat and/or oil by means of alcoholysis wherein, in order to carry out the alcoholysis, an alkanol, in particular a monohydric alkanol, is added in excess to the fat and/or oil to be transesterified, characterised in that at least one alkanol fatty acid ester is added to the fat and/or oil in a quantity such that the reaction mixture produced thereby consists of one phase under the reaction conditions.

Surprisingly, it has now been found that merely a quite small quantity of added alkanol fatty acid esters can achieve this object. The addition of the alkanol fatty acid esters may take place before, after or at the same time as the addition of the alkanol.

In the process according to this invention, the initial stage in the transesterification is avoided or shortened, for example, in the case of alcoholysis using methanol, by adding a portion of the continuously produced methyl esters to the triacylglyceride starting product in quantities such that the mixture of oil, methanol and methyl esters consists of one phase. If the reaction mixture is in the form of one phase, the active alkanol concentration is high from the very beginning and the reaction proceeds correspondingly rapidly. For example, at 135°C, in the initial stage of a process heterogeneously catalysed by zinc arginate (production of methyl esters from palm oil), a reaction rate of 0.8 g/skg_{Znarg} was recorded and, after a single phase had formed, a reaction rate of 2.5 g/skg_{Znarg} was recorded.

The fat and/or oil used in the process according to the invention may, in particular, be of biological origin.

The quantity of alkanol fatty acid esters which has to be added in order to produce a one-phase mixture depends on the quality of the oil, the amount of the excess of alkanol and the reaction temperature. The excess of alkanol is generally added in an equivalent ratio (i.e. ratio of mol fatty acids in the fat and/or oil to mol monohydric alcohol) of 1:6 or more to increase the reaction rate and the yield of fatty acid alkanol esters.

Alkanol fatty acid esters preferably introduced into the process are, for example, methyl esters, ethyl esters and/or propyl esters.

The alkanol fatty acid esters are added preferably in a quantity of 5 to 50 wt.%, particularly preferably 12 to 20 wt.%, based on the fat and/or oil.

The process according to the invention is particularly effective if it is intended to carry out the transesterification in a heterogeneously catalysed process, which is preferably continuous. But the process according to this invention is advantageous even in the case of a homogeneously catalysed process, because the costs of vortexing the two phases in the initial stage of the reaction can be saved. Such heterogeneously catalysed processes are described, for example, in the above-mentioned DE 199 50 593.

Thus, in another preferred embodiment, a catalyst, which may be either a soluble catalyst or a metal salt of an amino acid or of an amino acid derivative which is insoluble in alkanols and in the reaction mixture, is added to the process.

The dissolved catalyst may, for example, be dissolved alkali metals or alcoholates of alkali metals.

The insoluble catalyst may contain a metal component, which is calcium, strontium, barium, another alkaline-earth metal, or a heavy metal, in particular silver, copper, zinc, manganese, iron, nickel, cobalt, lanthanum or another rare-earth metal, while the amino acid component of the insoluble catalyst may contain quaternary nitrogen or a guanidino group. The insoluble catalyst is particularly preferably a heavy metal salt of arginine, in particular the zinc salt or the cadmium salt of arginine. Here, the catalytically active salts which are insoluble in the reaction mixture can be deposited onto a suitable support.

The process according to the invention is carried out particularly effectively if the content of free fatty acids in the fat and/or oil to be transesterified is less than 0.5 wt.%, in particular less than 0.1 wt.%.

It has also been found that the reaction temperatures during the heterogeneously catalysed transesterification should be preferably within the range of 80°C to 160°C, in particular within the range of 100°C to 150°C.

Particularly preferably, the process according to the invention is a procedure which includes the recirculation of the alkanol fatty acid esters which remain behind as bottom product following separation of the glycerol from the product flow during the subsequent separation and purification by distillation of the bulk of the methyl esters produced. In this way, small quantities of unreacted glycerides are simultaneously recirculated. Moreover, the glycerol content in the final stage of the

reaction is thereby lowered and the yield of the equilibrium reaction is correspondingly increased. Overall, a continuous operation is thus rendered possible.

5 The preferred quantity of methyl esters for producing a single phase at reaction temperatures within the range of 100°C to 150°C is approximately 12 to 20 wt.%.

Below, the process according to the invention is explained in more detail by several examples.

10 Thus, the process according to the invention was tested on a mixture of sunflower oil and methanol. In this case, at 135°C and with an equivalent ratio of mol fatty acids in the oil to methanol of 1:6 (60 wt.% sunflower oil and 40 wt.% methanol), an addition of approximately 15 wt.% methyl esters, based on the oil, was sufficient to produce a one-phase system. The pressure established in the case described was
15 5 bar. Zinc arginate was used as catalyst. The reaction rate was 2.5 g/skg_{Znarg}. In this Example, a high reaction rate was maintained from the beginning.

20 In addition, palm oil was mixed with methanol at 150°C in an equivalent ratio of 1:6 and zinc arginate was added as catalyst. After the addition of 20 wt.% methyl esters, based on palm oil, the mixture consisted of one phase. At 3.2 g/skg_{Znarg} the reaction rate was high from the beginning. The initial stage with a low reaction rate was omitted.

25 Palm oil was also mixed with methanol at 85°C in an equivalent ratio of 1:6 and zinc arginate was added as catalyst. The reaction rate was 0.05 g/skg_{Znarg}. After a one-phase reaction mixture had been produced by the addition of methylesters (approximately 13 wt.% based on oil), a reaction rate of 0.35 g/skg_{Znarg} was recorded at ambient pressure.

30 At reaction temperatures of 200°C to 240°C, in accordance with the process described in the German Patent DE 198 03 053 C1, using zinc soaps as catalysts at pressures of up to 90 bar, triglycerides were converted to esters with a high equivalent excess of methanol (equivalent ratio greater than 1:6). Under these conditions, a higher content of methyl esters is required to produce a onephase system than in
35 the above example at 135°C.